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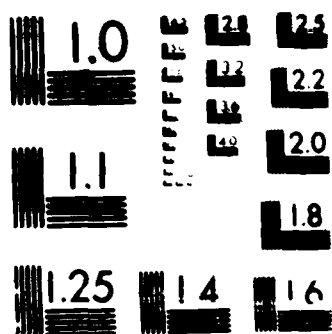
A STUDY OF VARIABLES THAT AFFECT RESULTS IN THE ASTM
D2274 ACCELERATED ST. (U) DAVID W TAYLOR NAVAL SHIP
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David W. Taylor Naval Ship Research and Development Center

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DTNSRDC/SME-86/77 April 1987

Ship Materials Engineering Department

Research and Development Report

A STUDY OF VARIABLES THAT AFFECT RESULTS IN THE
ASTM D2274 ACCELERATED STABILITY TEST

Part I: Laboratory, Operator, and Process
Variable Effects

by

Dr. E.W. White

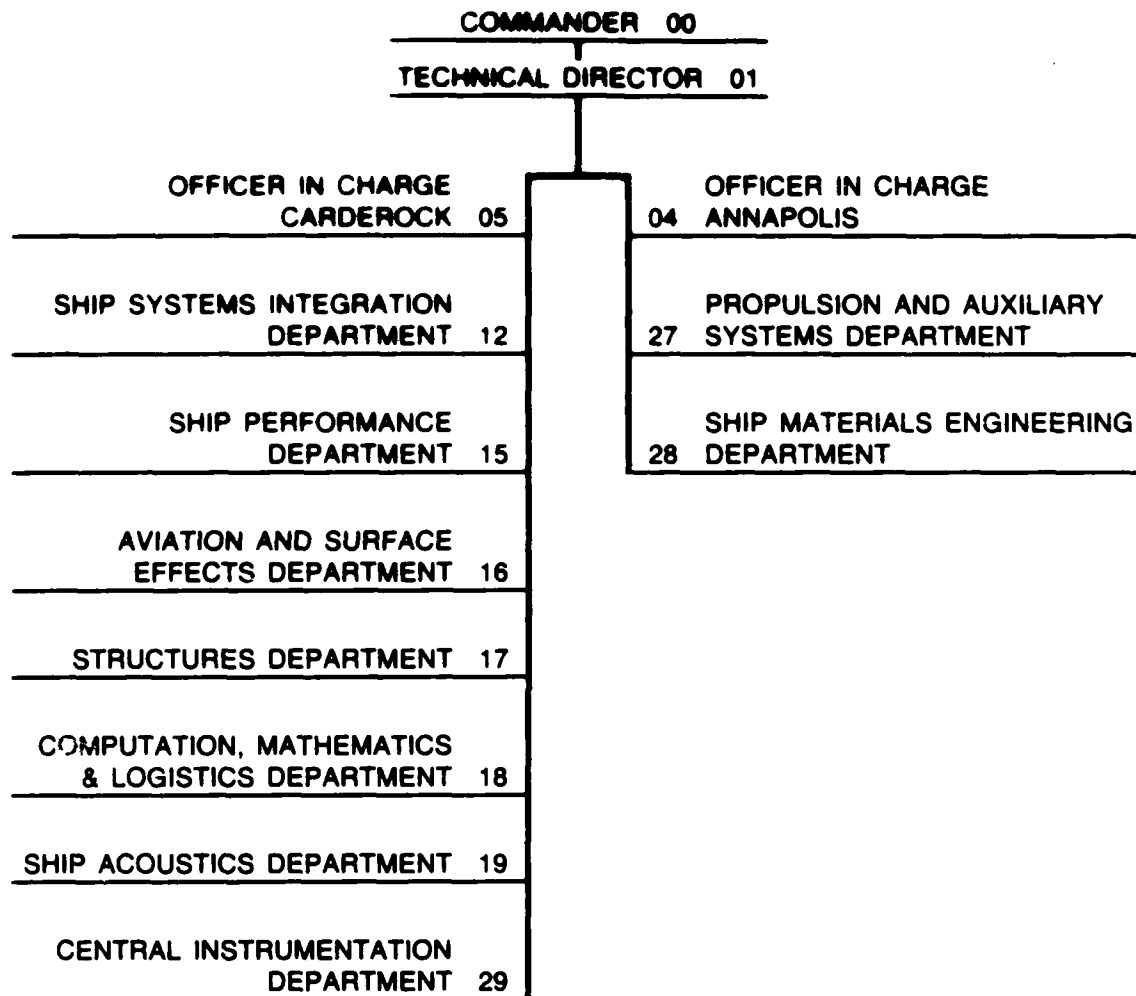
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DTNSRDC/SME-86/77 A Study of Variables that Affect Results in the ASTM D2274
Accelerated Stability Test Part I: Laboratory, Operator, and Process Variable Effects

STANDARDIZED TECHNICAL COMPONENTS



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SECURITY CLASSIFICATION OF THIS PAGE

AD-1180 209

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b RESTRICTIVE MARKINGS	
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION AVAILABILITY OF REPORT	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE			Approved for public release; distribution unlimited.	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) DTNSRDC/SME-86/77			5 MONITORING ORGANIZATION REPORT NUMBER(S)	
6a NAME OF PERFORMING ORGANIZATION David Taylor Naval Ship R&D Center		6b OFFICE SYMBOL (if applicable) DTNSRDC	7a NAME OF MONITORING ORGANIZATION David Taylor Naval Ship R&D Center (Code 2759)	
6c ADDRESS (City, State, and ZIP Code) Bethesda, MD 20084			7b ADDRESS (City, State, and ZIP Code) Bethesda, MD 20084	
8a NAME OF FUNDING SPONSORING ORGANIZATION Office of Naval Research		8b OFFICE SYMBOL (if applicable) Code 1232	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c ADDRESS (City, State, and ZIP Code) Arlington, VA 22217-5000			10 SOURCE OF FUNDING NUMBERS	
			PROGRAM ELEMENT NO 63724N	PROJECT NO R0838SL
			TASK NO R0838	WORK UNIT ACCESSION NO DN 278567
11 TITLE (Include Security Classification) A STUDY OF VARIABLES THAT AFFECT RESULTS IN THE ASTM D2275 ACCELERATED STABILITY TEST				
12 PERSONAL AUTHOR(S) Dr. E.W. White				
13a TYPE OF REPORT Research & Development		13b TIME COVERED FROM _____ TO _____	14 DATE OF REPORT (Year, Month, Day) 1987 April	
15 PAGE COUNT 49				
16 SUPPLEMENTARY NOTATION Part 1: Laboratory, Operator, and Process Variable Effects				
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP		
			Fuel Fuel Stability Procedure Differences	
			Navv Fuel ASTM D2274 Operator Differences	
			Diesel Fuel ASTM D2274 Variables	
19 ABSTRACT (Continue on reverse if necessary and identify by block number) <p>Poor reproducibility among laboratories that use the ASTM D2274 test for the storage stability of distillate fuels has long been a problem. Different operators who use the same equipment obtained different average results even within a single laboratory. A questionnaire relating to the method was sent to users to elicit information about variations in practice among laboratories and to gain insight into the causes. This Center began a task to identify the critical variables in the test procedure. We tested three fuels and concluded that there is negligible effect from variations in the bath temperature of less than 0.2°C (32.4°F), in oxygen flow rate of less than 0.3 L/hr, and of time-in-bath of less than 0.25 hr. However, each of these variables (especially the temperature) has a major impact if the limits are exceeded.</p>				
20 DISTRIBUTION AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. E.W. White			22b TELEPHONE (Include Area Code) (301) 267-2860	22c OFFICE SYMBOL Code 286

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted

All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

U.S. Government Printing Office: 1985 539-012

0102-LF-014-6602

UNCLASSIFIED

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE



UNCLASSIFIED

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ABBREVIATIONS

°API	Gravity by American Petroleum Institute scale
ASTM	American Society for Testing and Materials
°C	Degrees Celsius
cm	Centimeters
cSt	Centistokes
Cu	Copper
°F	Degrees Fahrenheit
FIA	Fluorescent indicator adsorption
GC	Gas chromatography
HPLC	High-pressure liquid chromatography
Hz	Hertz
LCO	Light-cycle oils
L/hr	Liters per hour
μm	Micrometers
mg KOH/g	Milligrams of potassium hydroxide per gram
mg/mL	Milligrams per milliliter
mL	Milliliters
mm	Millimeters
OD	Outside diameter
ppm	Parts per million
SD	Standard deviation
SR	Straight run
SWRI	Southwest Research Institute
TAN	Total acid number
wt	Weight

ABSTRACT

Poor reproducibility among laboratories that use the ASTM D2274 test for the storage stability of distillate fuels has long been a problem. Different operators who use the same equipment obtained different average results even within a single laboratory. A questionnaire relating to the method was sent to users to elicit information about variations in practice among the laboratories and to gain insight into the causes. This Center began a task to identify the critical variables in the test procedure. We tested three fuels and concluded that there is negligible effect from variations in the bath temperature of less than 0.2°C (0.4°F), in oxygen flow rate of less than 0.3 L/hr, and of time-in-bath of less than 0.25 hr. However, each of these variables (especially the temperature) has a major impact if the limits are exceeded.

ADMINISTRATIVE INFORMATION

The work described in this report was conducted over a period of 3 fiscal years as part of the Navy Energy Program - Fuels Chemistry. The work was performed under Program Element 63724N, Task Area Z0838 (Center Work Unit 1-2705-172 for FY 1983, 1-2705-212 for FY 1984 and 1-2759-313 for FY 1985), and was funded by the Naval Material Command, Code 08E (Dr. Alan Roberts and Mr. Wayne Vreath). The program was block-funded to this Center with Dr. C. F. Krolick (Code 275) as the Block Program Manager, and Mr. R. Strucko (Code 2759) as the Project Engineer. Dr. E.W. White (Code 2832) served as the Technical Manager for the Center.

INTRODUCTION

The American Society for Testing and Materials (ASTM) Method D2274 for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)¹ represents an effort to produce reactions in the relatively short time of 16 hr, which take much longer in normal storage at ambient temperature. This test method has been criticized as having poor precision and reproducibility, and as having an uncertain relationship to the development of insoluble substances during storage. However, despite its limitations, ASTM D2274 effectively kept unstable fuel out of the Navy's Naval Distillate Fuel system prior to 1981.

The test consists of aging a 350-mL volume of filtered fuel at 95°C (203°F) for 16 hr while oxygen is bubbled through the fuel at a rate of 3.0 L/hr. After the aged fuel has been cooled to ambient temperature (22.2° to 25.6°C (72° to 78°F)), it is filtered to separate filterable insolubles which are rinsed with knock-engine grade isooctane, dried, and weighed. Insolubles that adhere to the oxidation cell and associated glassware are removed by a solvent that consists of equal volumes of methanol, acetone, and benzene; the solvent is evaporated; and the remaining adherent insolubles are weighed. The sum of the filterable and adherent insolubles is reported as the total insolubles.

This test is the only standardized method to test the storage stability of distillate fuels and is used, despite its limitations, in several government specifications to preclude the acquisition of highly unstable fuels. The Army uses it in Federal Specification VV-F-800, Fuel Oil, Diesel, and the Navy uses it in Military Specification MIL-F-16884 Fuel, Naval Distillate.

The Army specification limits the total insolubles as measured by ASTM D2274 to a maximum of 1.5 mg/100 mL. The Navy specification originally limited total insolubles to 2.5 mg/100 mL, but this limit was reduced to 1.5 mg/100 mL in the current version of the specification, MIL-F-16884H of 3 May 1983.

The method was developed in principal at the Center in the late fifties and early sixties, at a time when the Navy was considering the use of catalytically cracked material in its fuel. Previously, the Navy insisted on straight-run (SR) distillate only. The method then was standardized by the American Society for Testing and Materials. In the early seventies, the results of an interlaboratory test showed that the total insolubles measured by the method had a repeatability of 0.3 mg/100 mL and a reproducibility of 1.0 mg/100 mL for total insolubles in the range of 0 to 1.0 mg/100 mL.

ASTM Committee D02 on Petroleum Products and Lubricants uses repeatability and reproducibility as precision measures that relate to a single operator and to

different operators in different laboratories, respectively. Specifically, repeatability is defined as the difference between two test results at the 95% confidence level when those results are determined by a single operator in a given laboratory using the same apparatus under constant operating conditions on identical test material. Reproducibility is defined as the difference between two single and independent results at the 95% confidence level, when the single results are obtained by different operators in different laboratories and when the same test method is applied to identical test samples. These values are related to the repeatability standard deviation and to the reproducibility standard deviation, respectively.

BACKGROUND

In late 1980 and early 1981, the Navy experienced a series of ship problems traced to an unstable fuel that had passed the 2.5 mg/100 mL total insolubles limitation in effect at that time. Nozzles plugged and filter/coalescer elements had to be replaced after very short periods of use.

Samples of the fuel were examined at the Center; at the Naval Research Laboratory (NRL), Washington, DC; and at the Naval Ship Systems Engineering Station, Philadelphia, PA. It was concluded that:

- The sediment in the fuel was largely organic in nature (possibly carboids).
- Microbial contamination was not the major problem.
- The dominant base stock in the fuel was a catalytically cracked product.
- Some of the test fuel had ASTM D2274 total insolubles in the range of 3.2 to 3.9 mg/100 mL (i.e., well in excess of the 2.5 mg/100 mL specification limit).

These findings indicated that the use of large quantities of cracked stocks by the refinery had possibly resulted in an unstable fuel that yielded organic insolubles

during storage. This was supported by a report in the technical literature that the refiner included some residual stocks in the feed to the catalytic cracking unit. The need for further research was recognized by the Navy Petroleum Office and the Naval Sea Systems Command. In early May 1981, this Center was tasked to develop a formal R&D program to determine the cause of and a solution for the problem with unstable fuel.

In response, we noted that technical forecasts indicated that a higher percentage of the total crude processed in future years would be of the heavier crude type. These would contain higher levels of nitrogen and sulfur, elements which are present in some of the more unstable compounds in fuels. Moreover, to produce the volumes of distillate fuels anticipated, it would be necessary to upgrade the heavy residuum from such crudes by hydrocracking, coking, visbreaking, and inclusion in catalytic cracking unit feedstocks. In short, the nature of the fuels the Navy would receive could be expected to be of poorer quality than those used currently.

Our proposed R&D program included two sections directed at the determination of the fuel's storage stability. The first was to investigate the reasons why the fuel had passed the ASTM D2274 test when the fuel was actually quite unstable. The second was to develop a suitable test for inclusion in the MIL-F-16884 specification to preclude acceptance of unstable fuels.

As part of the effort to determine why the fuel had passed the ASTM D2274 test when it was unstable, this Center and a contractor ran a variety of tests to fingerprint both the unstable fuel and a reportedly stable fuel. We felt that differences between the stable and the unstable fuels may provide a basis for a test to prevent the introduction of unstable fuels into the Navy fuel system.

By the end of 1982, gross differences between two samples of the unstable fuel and two samples of known stable fuels had been identified. First, the bromine numbers of the unstable fuels, determined by ASTM D1159 "Method for Bromine Number of

Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration,"² were appreciably higher than those of the stable fuels (3.9 and 4.6 versus 0.6 and 0.8).

Second, the unstable fuels contained more aromatics and less saturates than the stable fuels as determined by ASTM D1319 "Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption (FIA)."² Although the FIA technique is not reliable for products with endpoints above 315°C (600°F), the major differences (33.5% to 37.5% aromatics versus 23.0% to 25.1%) and confirmation of the general differences by NRL using high-pressure liquid chromatography (HPLC) support the conclusions.

Third, the unstable fuels contained more asphaltines (190 and 224 ppm) and more bitumens (129 and 162 ppm) than did the stable fuels (66 and 84 and 80 and 0 ppm, respectively). Finally, the unstable fuels had much higher total acid numbers (TAN's) by ASTM D974 "Method for Neutralization Number by Color-Indicator Titration,"² than did the stable fuels (0.15 and 0.24 versus 0.02 and 0.03 mg KOH/g, respectively).

In addition to the "wet chemistry" tests noted above, a Center contractor examined the unstable fuels using a gas chromatograph (GC) equipped with a nitrogen detector; this was supplemented with a GC mass spectrometer study. The study revealed the presence of various aromatic nitrogen heterocycles including various alkyl imidazole isomers, pyrroles, and pyridines in the lower boiling fractions of the unstable fuels. The higher boiling fractions of both the stable and unstable fuels contained isomers of quinoline, isoquinoline, and substituted carbazoles.

When the quantities of elemental nitrogen were calculated from the previous data in conjunction with the specific gravity of each fuel, we found that the unstable fuel samples contained 2.5% to 2.9% nitrogen versus only 0.8% to 1.1% in the stable fuels. Further, we found that such heteroatoms tended to concentrate in the sediments formed during accelerated aging. The sediments from the unstable fuels contained

15.4% to 16.0% nitrogen and up to 1.79% sulfur. The sediments from a stable fuel contained only 2.9% nitrogen and 1.02% sulfur.

By late 1982, the Center initiated a program to develop an improved accelerated stability test. The first step was an experimental evaluation of the variables that affect the results obtained with the ASTM D2274 procedure. We felt that poor control of critical variables might explain the poor reproducibility associated with the method. A similar proposal was submitted to the Navy about the same time by the Southwest Research Institute (SWRI), which has extensive experience with fuel stability tests.

At a meeting in December 1982, it was decided that both SWRI and the Center could contribute to the study. In general, the Center addressed those variables involved in the aging process: the stressing temperature, the time the sample is kept at temperature, and the flow rate of the oxygen to the oxidation cell. SWRI addressed the variables involved in the postaging processes: the cool-down rate, the method of filtration, and the nature of the solvent used to remove adherent insolubles. SWRI also addressed the affect of the variables on the particle size distribution of the filterable insolubles.

In April 1983, the Quadripartite Navies expressed concern over the inadequacy of test methods to measure the instability tendencies of ship fuels. Delegation leaders from the Royal Australian Navy, the Royal Navy, the U.S. Navy, and the Canadian Forces forwarded a letter to Mr. P.L. Strigner, chairman of ASTM Committee D02 on Petroleum Products and Lubricants, to request that the Committee place considerable emphasis on the improvement or replacement of ASTM D2274.

ASTM Committee D02 accepted this responsibility in June 1983 and an ad hoc committee of Section E-5 on Cleanliness and Stability was formed to develop plans. This group, which formed the nucleus of a joint task force of Sections 5-B on Oxidation of

Distillate Fuels and of Section E-5, first met at the Center on 18 and 19 October 1983. It was agreed that the quickest response to the needs expressed by the four Navies would be to improve the basic ASTM D2274 procedure.

NATURE OF REPORT

This report answers three questions concerning use of the ASTM D2274 procedure to evaluate the stability of fuels:

1. Do laboratories that employ this method actually use the same techniques and procedures?
2. Do operators in the same laboratory obtain the same results, or do operator differences contribute materially to the poor reproducibility of the method?
3. Are the specified primary variables (bath temperature, oxygen flow rate, and time-in-bath) major contributors to poor reproducibility, if they are kept within prescribed limits?

The first question is answered by an analysis of responses to a questionnaire issued in conjunction with the Center's October 1983 meeting of the ASTM ad hoc committee. The second is answered by an analysis of data obtained by five Center operators on the same fuel. The third is answered by data obtained by varying the test temperature, the oxygen flow rate, and the time-in-bath of three test fuels. The effect of time-in-bath is also discussed in conjunction with recent data obtained on two additional fuels.

DESCRIPTION OF EQUIPMENT AND MATERIALS

GENERAL INFORMATION

The Questionnaire on the Use of the ASTM Test for Oxidation Stability of Distillate Fuel Oil (Accelerated Method - ASTM D2274) was intended to identify differences in interpretation and practices among laboratories that use the method. The questionnaire was sent to ASTM members who expressed an interest in the work of the

ad hoc committee. They were requested to report what actually was being done in their laboratories, and not to provide a mere iteration of what is in the written procedure.

The questions (see Appendix A) were grouped with respect to major aspects of the procedure. For example, there were questions that dealt with samples and sampling, others covered reagents and materials, and still others examined the size and preparation of oxidation cells.

The laboratory investigations covered in this report extended over a period of several years. Some were designed to test, train, and evaluate the analysts used in the program. Others were designed to determine the effects of the specified process variables (bath temperature, oxygen flow rate, and time-in-bath).

The bulk of the laboratory work was subdivided into two distinct phases. The first phase was conducted in 1983 using a reputedly stable Naval Distillate Fuel received from one of the Navy supply depots. The second phase was conducted in 1984 and 1985 using two diesel fuels supplied by NRL.

Minimal laboratory work was conducted to determine the effects of time-in-bath on still other fuels furnished by NRL. Those fuels were either light-cycle oils (LCO) or blends of LCO's with straight-run distillate. Some of these fuels came from a Gulf-coast refinery; the balance came from a West-coast refinery.

DESCRIPTION OF D2274 OXIDATION UNITS

Work on the first three fuels, which represented the bulk of the laboratory work reported herein, was conducted in an 8-cell oxidation apparatus. The more recent work that will be cited briefly was conducted in a 12-cell oxidation unit.

Figure 1a shows the Lawler Manufacturing, Inc., 8-cell oxidation apparatus, Model 2274. The apparatus draws 9 amperes of current from a 115-volt, 60-Hz power supply.

Figure 1b shows the Koehler Instrument Company, Inc., 12-cell oxidation apparatus, Model K122-12A. It draws up to 16 amperes from a 230-volt, 60-Hz power supply. The heating bath contains a thermostatically controlled 750-watt heater and two 1500-watt heaters that can be turned on or off by a toggle switch.³

FUEL PROPERTIES

The three fuels used were all diesel-range fuels. The first, obtained from a Navy fuel depot, was a conventional MIL-F-16884 naval distillate fuel. The second consisted of 30% by volume of aged LCO and 70% good quality aged naval distillate fuel. The two stocks were furnished separately by NRL and blended in the desired ratio at the Center. The third fuel was an Army diesel fuel that conformed to Federal Specification VV-F-800 for Fuel Oil, Diesel. This fuel was obtained by NRL from an Army base in the continental United States (CONUS). Some chemical and physical properties of these fuels are given in Table 1.

Table 1. Selected properties of three test fuels.

Property	Fuel N	Fuel A	Fuel B
Gravity, °API, 15.6°C	39.0	31.1	35.0
Viscosity, cSt, 40°C	3.4*	NA**	2.3
Color (ASTM)	NA	L3.5	2.5
Flash Point, °C	80	>60	77
Pour Point, °C	NA	NA	-31
Cloud Point, °C	NA	NA	-21
Distillation, °C			
50% Point	286	276	256
90% Point	340	339	302
End Point	366	360	330
Copper Strip at 100°C	No. 1b	NA	No. 1
Carbon Residue (10% bot), %	0.09	NA	0.05
Sulfur, % (wt)	0.52	NA	0.40
Ash, % (wt)	NA	NA	0.003
Acid Number, mg KOH/g	0.02	NA	0.02
Accelerated Stability, mg/100 mL	3.9	2.4	3.1
*Measured as 3.5 cSt at 38°C. **NA - Not available.			

Tests conducted for the Center indicated the first fuel (Fuel N in Table 1) consisted of about 75% saturated compounds, 2% olefinic compounds, and 23% aromatic compounds, and was probably a blend of straight-run and catalytic stocks in a ratio of about 9:1. Information on the other two fuels (A and B in Table 1) obtained at NRL by HPLC indicated that Fuel A consisted of about 67% saturates, 21% monocyclic aromatics, and 12% dicyclic and polycyclic aromatics. Fuel B was intermediate in saturates (71%), and contained 19% monocyclic aromatics, and 19% dicyclic and polycyclic aromatics.

The properties of LCO's and SR distillates used in recent work are reported by White.⁴ The Gulf-coast fuels had viscosities of 3.04 to 3.28 cSt at 40°C (104°F), API gravities from 26.4 to 37.7, sulfur contents of 0.32% to 0.34%, and distillation end point temperatures of 329° to 338°C (624° to 640°F). The West-coast fuels had viscosities of 2.62 to 3.63 cSt at 40°C (104°F), API gravities from 17.0 to 33.7, sulfur contents of 0.47% to 0.98%, and distillation end point temperatures of 323° to 332°C (614° to 630°F).

PROCEDURES

QUESTIONNAIRE

The questionnaire (Appendix A) was mailed to ASTM members who expressed an interest in the planned work of the ad hoc committee. Ten responses were received. All of the respondents did not answer every question. All of the answers were tabulated and analyzed for similarities and differences in the way the method is practiced at the responding laboratories. Differences were evaluated with respect to their potential effects on the results; i.e., differences were examined to determine whether the effect on the measured values of insolubles would be major or minor.

OPERATOR EFFECTS

The Center makes considerable use of qualified co-op students and summer hires. Consequently, a number of different operators were used in the course of the work. Operators were asked to run a set of eight oxidation cells according to the ASTM D2274 procedure and to determine the standard deviation of their results, in an effort to help the operator develop technique and to check the repeatability of the data.

Five operators completed the 8-cell set using Fuel N during the period January 1983 through January 1984. These individuals will be referred to as Analysts A through E. Analysts A and C ran two sets of eight cells; the others ran only one set.

The five analysts had diverse backgrounds and experience. Analysts A and E were co-op college students who were chemistry majors. Analyst A had conducted the test a number of times in the past, whereas Analyst E was running the test for the first time. Analyst B was a college student, but not a chemistry major. She worked during the summer at the laboratory and was quite familiar with the method. Analyst C was a college professor who works for the Center during the summer; he had not run the method prior to the first set of eight. Analyst D is a full-time, experienced, degreed chemist who had been transferred recently from another area of work and had not run the method previously. He deviated from the method by running a blank and correcting values on the basis of the blanks.

PROCESS VARIABLE EFFECTS

Fundamentally, ASTM D2274 specifies only three process variables -- the bath temperature, the flow rate of oxygen to the oxidation cell, and the time the oxidation cell and its contents are kept in the temperature bath. The bath temperature must be set high enough to maintain the fuel in the oxidation cell at $95^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ($203^{\circ} \pm 0.4^{\circ}\text{F}$). In practice, it is the bath that is maintained at 95°C (203°F). The oxygen

flow to each cell must be adjusted to 3 ± 0.3 L/hr. The flowmeter used to measure the flow rate is to have an accuracy of ± 0.3 L/hr, but no calibration step is indicated. The oxidation cells that contain fuel to be tested must be kept in the heating bath for 16 hr. No deviation in time is indicated and, in practice, the cells can be removed within a few minutes of the specified time.

Operating temperatures of 85°, 95°, and 105°C (185°, 203°, and 221°F) were used in the early work with Fuel N. Follow-on studies with Fuels A and B used temperatures of 80°, 95°, and 110°C (176°, 203°, 230°F).

Variations in the oxygen flow rate were the same in all phases of the program. Flow rates of 0, 1.5, 3.0, and 4.5 L/hr were used. In the zero flow rate condition, the fuel was exposed to the supernatant layer of air and air could diffuse into the oxidation cell through the condenser opening, but there was no positive introduction of oxygen through the normal oxygen delivery system.

Time-in-bath variations ranged from 4 to 32 hr, but were not necessarily the same in any two batches of eight cells. During the early work with Fuel N, batches at 85° and 105°C (185° and 221°F) involved duplicate determinations at 4, 8, 16, and 24 hr. A third batch, at 95°C (203°F), involved duplicate determinations at 4, 8, 24, and 30 hr. (The 16-hr determination was skipped because it had been measured previously.) In later studies with Fuels A and B, duplicate determinations were made at 4, 8, 16, and 32 hr at each of the three temperatures (80°, 95°, and 110°C (176°, 203°, 230°F)).*

Data from the tests were used to draw curves of insolubles versus temperature, of insolubles versus oxygen flow rate, and of insolubles versus time in bath. The slopes of the curves were then estimated at the control points (95°C (203°F), 3.0 L/hr oxygen flow, and 16 hr in the bath). The estimated slopes were used to

*Recent work developed time versus insolubles curves out to 60 hr in the bath.

calculate approximate effects of deviations of $\pm 0.2^{\circ}\text{C}$ ($\pm 0.4^{\circ}\text{F}$) in bath temperature, ± 0.3 L/hr in oxygen flow, and ± 0.25 hr time-in-bath. The values of 0.2°C (0.4°F) and 0.3 L/hr are the deviations permitted by the ASTM D2274 procedure. The value of 0.25 hr was selected as a deviation that might be experienced in practice.

DISCUSSION OF RESULTS

SUMMARY OF QUESTIONNAIRE RESPONSES

Questionnaires returned indicated that some of the respondents used the procedure on No. 2 fuel oil, some used it on diesel fuels, and some used it on other fuels.

Samples and Sampling

ASTM D2274 specifies that samples are to be stored in metal cans which have been cleaned with adherent insolubles solvent and then rinsed with the sample. (Clear glass bottles are stated to be unsatisfactory.) A sample that cannot be tested immediately is to be stored under nitrogen at a temperature no higher than 10°C (50°F) and is not to be held longer than 1 week.

In reality, samples were obtained from a variety of sources: refinery, shipping terminal, customs office, laboratory-prepared blend, or 55-gallon (208.2-liter) drum used for other tests. Several laboratories indicated the source of the sample was unknown.

Several respondents indicated they did not know the age of the sample. One said the sample was run within 1 week of receipt. Two respondents indicated the age of the sample was 3 months; others ranged from fresh to 2 years, from 3 days to 2 years, or were a monthly composite.

The sample containers used included 1- and 5-gallon (3.8- and 18.9-liter) metal cans, 55-gallon (208.2-liter) drums, 0.3-gallon (1-liter) cans, 1-gallon (3.8-liter) Teflon[™]-coated cans, and glass bottles (contrary to the instructions given in ASTM D2274).

[™]Teflon is a trade name of E.I. du Pont de Nemours and company.

The storage locations and temperatures of storage varied also. Some were stored in cold storage rooms at 4.4°C (40°F), but others were stored in the laboratory, on the bench, or in a storage building at ambient temperatures that ranged from 18° to 24°C (64° to 75°F). Three respondents indicated use of a nitrogen blanket, and one of these indicated that nitrogen normally was not used.

Reagents and Materials

The method does not specify the oxygen purity. Respondents indicated the use of a wide variety of oxygen-containing gases from lab-filtered, compressed air through industrial grade, 99+%, and 99.5% grade oxygen. The use of compressed air is not within the scope of the method, which specifies a tank of oxygen.

The method specifies that the hydrocarbon solvent shall be prefiltered isooctane of ASTM knock-test reference fuel grade. The use of a number of other solvents as hydrocarbon solvent was also reported. One respondent used commercial grade Skelly BC™ (not an isooctane); another used industrial grade Quimex (hexane). The others all used isooctane that was ASTM or knock-test grade, or Fisher lab grade. Most respondents prefiltered whatever hydrocarbon solvent they used, but two did not.

ASTM D2274 states that the adherent insolubles solvent shall be a mix of equal parts reagent grade benzene, methanol, and acetone. One respondent occasionally used benzene to prepare the adherent insolubles solvent. The others used toluene, probably to escape the toxic properties of the benzene. Similarly, the bulk of the toluene responses indicated the use of reagent grades, but two reported the use of commercial or technical grade material.

One respondent reported the use of technical grade solvents. The others used methanol that was ACS, reagent, analytical anhydrous, Baker absolute, or analytical

™Skelly BC is a trade name of the Getty Refining and Marketing, Company, Tulsa, OK.

reagent grade. Most used similar reagent grades of acetone, but four used commercial, industrial, or technical grade products.

The procedure does not specify the glass-fiber filter paper to be used, but that of H. Reeve Angel and Company, Catalog No. X-934-AH, is stated to be satisfactory. Two respondents did not use glass-fiber filter paper, but used Millipore™ filters, one of which had 0.8- μ m pore size vis-a-vis the nominal 1.5- μ m openings of the Angel 934-AH paper. The other respondents used glass-fiber filter paper, either Angel or Whatman 934-AH grade, or Whatman GF/A grade with a 1.6- μ m pore size.

Oxidation Cells

It is specified that the oxidation cells are made of borosilicate glass with the dimensions shown in ASTM D2274, Figure 1, e.g., 600 mm long with a 45-mm OD. New cells are to be cleaned with chromic acid and used cells with water and detergent, followed by ASTM precipitation naphtha.

Respondents found general conformance to the specified cell dimensions, although several oxidation cells were reported to be 605 or 610 mm long vis-a-vis the specified 600 mm, with a 40-mm OD vis-a-vis the specified 45 mm.

Cleaning of oxidation cells seems to be an "every lab for itself" proposition. Some labs use chromic acid cleaning on new cells; some do not. Some rinse with tap water, some with distilled water. A wide variety of detergent brands are used. The precipitation naphtha rinse is often omitted, and when it is used, may involve 50- to 250-ml volumes. Chloroform, ether, hydrocarbon solvent, adherent insolubles solvent, or acetone were other solvents used to clean apparatus.

[™]Millipore is a trade name of the Millipore Corporation, Bedford, MA.

Gooch Crucibles

The method specifies the use of porcelain No. 4 Gooch crucibles, which should be cleaned with water and detergent followed by ASTM precipitation naphtha. Two glass-fiber filter disks are placed in the Gooch crucible and washed with 200 mL of isooctane poured into the crucible.

All respondents used porcelain crucibles except those who used a Millipore filter. Several used No. 3 crucibles rather than the specified No. 4 size. Top diameters of the crucibles ranged between 35 and 40 mm, and bottom diameters ranged between 23 and 25 mm. The number of holes in the bottom of the crucible varied from 37 up to 115. The approximate diameters of the holes in the bottom ranged from 0.5 to 1 mm.

Cleaning procedures varied widely. One respondent reported the use of chromic acid; another used soap and water, then soaked in acid for 4 hr. Several used water and detergent, then rinsed with either hot water or distilled water. One used Shell X-2 solvent rather than a water rinse after the water and detergent step. Several used solvent rinsing as the initial step. One of these respondents used trisolvant without further steps; the other used acetone, followed by soap and water, then oven-drying.

Volumes of isooctane used to rinse the filter disks ranged from 100 to 200 mL; the majority favored the specified 200-mL volume. Most respondents dried the Gooch crucible in an oven for 1 hr, one for 1 to 2 hr. Most cooled the crucible in a desiccator for 1 hr, one for 1 to 4 hr, and one overnight. All of the respondents used the two filter disks as specified, except those who used the Millipore filter.

Starting the Test

The method specifies that the fuel to be tested be placed in a 500-mL separatory funnel, from which it filters through a Gooch crucible that contains two glass-fiber

filter papers. There are no constraints on the length of time the filtered fuel may sit before it is placed in the oxidation cells or into the heating bath.

The various respondents filtered amounts of fuel that ranged from 350 mL (the amount to be placed in the oxidation cell) to 3000 mL, or as needed. Four of the responses to this question indicated either 350 or 375 mL, one indicated 500 mL, and one indicated 730 mL (stated to be for duplicate determinations). The respondent who filtered 3000 mL noted that this was for eight determinations; the respondent who filtered as needed indicated the volume was adjusted depending on the number of determinations to be made.

Five of the responses to this question indicated that a separatory funnel setup was used to conduct the filtration, as specified in the method. One of those who did not use this technique poured directly into the Gooch crucible; a second poured from a graduated cylinder; a third filtered straight from a can using the same setup but without the separatory funnel, since the sample was a very clear diesel fuel with no sediment.

After filtration, the fuel apparently was allowed to sit for 5 to 10 minutes or as long as 4 hr. One response was "same day, always", which could be interpreted to mean that it sat longer than 4 hr. Generally, 1 to 2 hr elapsed before the oxidation cells that contained fuel were placed in the temperature bath.

Temperature Stress Period

ASTM D2274-74 specifies that 350 ml of fuel in an oxidation cell shall be placed in a 95°C (203°F) temperature bath for 16 hr while oxygen is bubbled through the fuel at a rate of 3 ± 0.3 L/hr.

Eight respondents indicated that the oxidation cells remained in the temperature bath for the specified 16 hr \pm 5 minutes. Most bath temperatures were as specified,

95°C (203°F), but one respondent measured the temperature at 96.7°C (206°F) and one measured 98.9° to 100°C (210° to 212°F).

The respondents maintained the oxygen flow at 3 L/hr, but admitted that the instruments used to measure the flow had not been calibrated for periods that ranged from 1 month to over 2 years. With one exception, the respondents did not know the barometric pressure in the room where the test was being conducted. (The exception reported 1009 without specifying units.) Only one respondent knew the number of bubbles of gas released through the fuel sample (550 bubbles per minute). All apparently used the specified oxygen delivery tube.

Cooling Period

The method specifies that the oxidation cells shall be removed from the 95°C (203°F) bath at the end of the 16-hr period, and the samples shall be allowed to cool in the dark in a ventilated atmosphere with a temperature range of 22° to 27°C (72° to 80°F). The fuel temperature is to be checked after 4 hr and the test is to proceed if the temperature is within the specified 22° to 27°C (72° to 80°F) range. Otherwise, the sample must be allowed to cool an extra 1/2 hr.

The respondents indicated that the oxidation cells were placed in the dark or in subdued light after taking from 1 to 15 minutes to remove them from the bath. One respondent had a special box in the lab for such storage. Another placed the cell in a hood in subdued light, while another used a hood but covered the oxidation cell rack. One placed the oxidation cells in the filtering room, but did not indicate how much light could impinge on the cells.

All of the storage temperatures reported met method requirements, and all of the samples reached the specified final temperature within 4 hr. None of the respondents allowed more than 4 hr for cooling.

Determining Filterable Insolubles

The method specifies that the fuel sample be transferred to a separatory funnel after cooling; from there it is to be fed to a tared Gooch crucible for filtration. The oxidation cell and the oxygen delivery tube assembly are to be washed with three rinsings (about 50 mL each) of hydrocarbon solvent (isooctane). The separatory funnel must be rinsed similarly when filtration is completed. Then, all washings must be passed through the filter. The crucible then must be oven-dried for 1 hr, cooled in a desiccator, and weighed.

The specified filtration arrangement was used by only half the respondents. The procedures used to rinse the equipment with hydrocarbon solvent varied widely. One respondent used two rinses, and two used three or four. Volumes of solvent used per rinse varied from 15 to 20 mL up to 50 to 100 mL; most used approximately 50 mL.

The methods used to ensure contact between the glassware and the hydrocarbon solvent were different for each laboratory that responded. One reported rolling the tube (oxidation cell) after a stream of the solvent was sprayed over the entire surface. Another used a squeeze-type wash bottle to contact the tube while it was rotated. Another swirled the solvent around the tube manually. One rinsed with hexane rather than isooctane, and let the solvent drain along the edge of the tube. One reportedly "rinsed" only the crucible three times with hydrocarbon solvent, followed by jet evaporation via ASTM D381.

The quantities of solvent used to rinse the various pieces of equipment were reported as follows:

- 5 to 25 mL to rinse the glass funnel.
- 10 to 100 mL to rinse the separatory funnel.
- 150 mL to rinse the oxygen delivery tubes.
- 0 to 150 mL to rinse the outside of the Gooch crucible.

It took respondents 5 to 30 minutes to filter the test sample after cooling. Most respondents oven-dried the crucible for 1 hr, but one respondent indicated 1 to 1.5 hr, and one indicated 3 hr. Oven temperatures for that drying operation ranged from 65.6° to 110°C (150° to 230°F); most responses indicated the 93.3° to 98.9°C (200° to 210°F) range.

Adherent Gum Procedure

ASTM D2274-74 specifies recovery of adherent gum (now frequently referred to as adherent insolubles) through the use of adherent insolubles solvent, a.k.a. trisolvent. The oxidation cell and associated glassware, which have been rinsed with hydrocarbon solvent to remove residual volumes of fuel, are rinsed with the trisolvent to dissolve adherent gum. The solvent is removed by evaporation at 160°C (320°F) by the air jet method described in ASTM D381, "Test for Existent Gum in Fuels by Jet Evaporation."²

The volume of adherent insolubles solvent is not specified. Respondents indicated the use of 50 to 150 mL distributed among two to four separate rinses. Application techniques paralleled those used to apply the hydrocarbon solvent rinses. The use of wash bottles to direct a stream of solvent while rotating the equipment so as to contact all surfaces was typical. There was seldom evidence of color left on the glassware after the trisolvent rinses. One reported, "not usually;" others said no color was evident.

Six respondents used the ASTM D381 air jet procedure as specified. Two respondents used other methods to evaporate the solvent. One put the beaker in an oven at 110°C (230°F); the other put the beaker on a steam bath. Most respondents used filtered air to prevent scale and other debris from the compressed air system from getting into the beakers. One trusting individual indicated there was no extraneous material in the air supply.

Repeatability and Reproducibility

Respondents were asked several questions to ascertain their observations regarding the poor precision associated with the D2274 method.

First, they were asked whether they ran duplicate determinations to improve the precision of their results; two normally did, three occasionally did, and two never ran in duplicate.

Second, those who ran duplicates were asked their experience with duplicate results. Answers were given in two ways -- as \pm mg/100 mL and as \pm a percentage. Duplicate determinations of filterable insolubles fell in the 0.1 to 0.5 mg/100 mL range or in the 5% to 22% range. Duplicate determinations of adherent gum fell in the 0.3 to 0.5 mg/100 mL range or from less than 5% to 32%. Duplicate determinations of total insolubles fell in the 0.1 to 0.5 mg/100 mL range or in the 5% to 22% range.

Third, the questionnaire asked why reproducibility was poor among laboratories. Respondents cited such factors as differences in sample handling, differences among operators, and not following the method. Respondents also pointed out that the product was an unstable one, that there could be differences in the initial peroxide concentration, and that the test did not last long enough (was not severe enough) to achieve the full potential insolubles.

Laboratory

Respondents were asked questions about the physical arrangements and the environmental aspects of their individual laboratories.

Five indicated that the different parts of the test (filtering, temperature stressing, weighing, jet evaporation, and oven-drying) were conducted in the same room. Four indicated some of these operations were conducted in separate rooms.

Four respondents conducted tests in rooms that were exposed to sunlight; five indicated that sunlight was not a factor. Five indicated that temperatures in the

laboratory were approximately the same summer and winter; three said there were differences of 1.1° to 16.7°C (2° to 30°F). Day and night temperatures differed by 4.4° to 11.1°C (8° to 20°F).

Most respondents stated that the fuel samples were not exposed to sunlight during any part of the test, but three indicated some exposure.

Summary

The results of the questionnaire indicate some significant differences in interpretation and application of the method. We concluded that the method should be rewritten to emphasize the critical instructions.

OPERATOR EFFECTS

Variations in Total Insolubles

Table 2 summarizes test results obtained with the same fuel reported by five different individuals. The ranges, averages, and standard deviations shown in the table used all eight data points from each run. Even outliers were included for the first examination of the results. A few trials in which outliers were systematically deleted did not seem to cause a major change in the sense of the values.

One fact that stands out is: there is a wide variation among the different analysts. Further, this variation is not a function of the individual's experience in the field of chemistry, but it may be a function of the degree of prior experience with the method. The data from Analyst C yielded the highest sample standard deviation (0.67 mg/100 mL) during his first familiarization test in June 1983. However, this value was approximately halved to 0.29 mg/100 mL when he ran a second batch of eight in July 1983. In contrast, Analysts A and B, who had the most experience with the method, obtained standard deviations in the 0.14- to 0.18-mg/100-mL range; the most experienced laboratory chemist, Analyst D, obtained the lowest sample standard deviation (0.08 mg/100 mL).

Table 2. Variations in results obtained by different analysts
(total insolubles in mg/100 mL).

Analyst	Date	Range	Mean	Standard Deviation
A	Jan 83	1.37 - 1.89	1.62	0.18
B	May 83	1.58 - 2.03	1.80	0.14
C	Jun 83	0.23 - 2.24	1.06	0.67
C	Jul 83	2.13 - 2.98	2.55	0.29
A	Sep 83	1.60 - 2.00	1.75	0.14
D	Nov 83	1.11 - 1.37	1.24	0.08
E	Jan 84	1.06 - 2.94	1.53	0.59
All operators		0.23 - 2.98	1.65	0.57

Table 2 shows that the total insolubles data (taken as a whole) ranged from 0.23 to 2.98 mg/100 mL, averaged 1.65 mg/100 mL, and had an average standard deviation of 0.57 mg/100 mL. ASTM Committee D02 conducted round-robin, interlaboratory tests in 1964, 1972, 1978, and 1985 in an effort to establish repeatability and reproducibility values for the D2274 procedure. Our in-house tests with different operators are more similar to interlaboratory tests in different laboratories with different operators than they are to in-house tests with the same operator. Therefore, the resulting standard deviation should be compared with the standard deviation associated with the determination of reproducibility.

The 1964, 1972, and 1978 round-robins yielded reproducibility of 2.4 to 3.4 mg/100 mL for all fuels with total insolubles >1.0 mg/100 mL. The 1985 round-robin related the reproducibility to the average level of total insolubles; specifically, it is given as equal to 1.06 times the 0.25 power of the total insolubles. The reproducibility would be about 1.20 mg/100 mL for a total insolubles level of 1.65 mg/100 mL (the average obtained by Center operators).

The reproducibility is proportional to the student t-factor times the reproducibility standard deviation. The t-factor is dependent upon the degree of freedom; thus it is a function of the number of samples and laboratories involved in a round-robin test. Round-robin tests usually involve sufficient samples and laboratories for the multiplying factor, based on the t-factor, to fall in the range of 2.80 to 2.84. Consequently, the reproducibility, R, is approximately 2.8 times the standard deviation, SD. The equation can be rearranged, $SD = R/2.8$, and the reported range of reproducibilities (1.2 to 3.4 mg/100 mL) would result from standard deviations that ranged from about 0.4 to 1.2 mg/100 mL. Hence, the 0.57 mg/100 mL standard deviation obtained in Center studies appears to be consistent with past experience.

Variations in Filterable Insolubles

Table 3 summarizes the results obtained for filterable insolubles. The individual groups are listed in ascending order of the average value of the eight data points for filterable insolubles obtained by the analyst.

Table 3. Variations in results obtained by different analysts
(filterable insolubles in mg/100 mL).

Analyst	Date	Range	Mean	Standard Deviation
C	Jun 83	0.00 - 1.06	0.66	0.43
A	Jan 83	0.74 - 1.20	1.04	0.15
D	Nov 83	0.97 - 1.20	1.09	0.08
E	Jan 84	0.84 - 2.61	1.27	0.56
B	May 83	1.34 - 1.60	1.51	0.09
A	Sep 83	1.37 - 1.97	1.56	0.20
C	Jul 83	1.48 - 1.73	1.64	0.07
All operators		0.00 - 2.61	1.25	0.43

Wide variations among the analysts again are evident. Individual data points ranged from 0 to 2.61 mg/100 mL, and the averages of the groups of eight ranged from 0.66 to 1.64 mg/100 mL. The sample standard deviations obtained in the groups ranged from 0.07 to 0.56 mg/100 mL. Again, the experience factor was evident in the results of the college professor, Analyst C, whose July results yielded a much smaller sample standard deviation (0.07 mg/100 mL) than did his June results (0.43 mg/100 mL). Also, Analysts A, B, and D, with more experience, generally had better sample standard deviations (0.08 to 0.20 mg/100 mL) than the data from Analyst E and the first group of data from Analyst C.

Variations in Adherent Insolubles

Table 4 shows the variations in results obtained by the five analysts in the determination of adherent insolubles. The results of the seven groups of eight are arranged in ascending order of the average levels.

Table 4. Variations in results obtained by different analysts
(adherent insolubles in mg/100 mL).

Analyst	Date	Range	Mean	Standard Deviation
D	Nov 83	0.06 - 0.23	0.15	0.06
A	Sep 83	0.00 - 0.51	0.18	0.19
E	Jan 84	0.18 - 0.34	0.25	0.06
B	May 83	0.09 - 0.43	0.29	0.12
C	Jun 83	0.06 - 1.30	0.46	0.38
A	Jan 83	0.43 - 0.69	0.59	0.07
C	Jul 83	0.65 - 1.31	0.91	0.24
All operators		0.00 - 1.31	0.40	0.31

Again, there is a wide scatter of data. Analyst C had the least experience in this type of testing and the largest sample standard deviations (0.38 mg/100 mL in June and 0.24 mg/100 mL in July). However, the averages in Table 4 for adherent insolubles have a ratio of about 6:1; whereas the averages in Table 2 for the total insolubles and in Table 3 for the filterable insolubles had ratios of about 2.5:1 (highest: lowest). In short, the reproducibility between analysts is poorer for the determination of adherent insolubles than it is for either the filterable insolubles or the total insolubles.

One explanation for the poor reproducibility between analysts in the determination of the adherent insolubles lies in the adherent insolubles solvent used to remove the adherent insolubles from the oxidation cells and fittings. ASTM D2274-74 requires that the solvent consist of equal volumes of benzene, acetone, and methanol; it is sometimes referred to as trisolvent. In practice, many laboratories have replaced the benzene with toluene to reduce the associated hazards; the resulting solvent sometimes is called TAM. One of the analysts evaporated the solvent to obtain a blank value and found that the solvent left an appreciable residue which was traced to the acetone used to prepare the trisolvent. We concluded that differences among the solvents used by the several analysts may have caused the wide scatter shown in Table 4. Differences among the solvents used in interlaboratory programs may explain part of the poor reproducibilities among laboratories.

Statistical Tests

A computer software package was used to evaluate the significance of differences between the means obtained by each individual and the base case. The base case is the first conducted in the study and was run by Analyst A in January 1983. There were six comparisons with the base case including the September 1983 set of data run

by Analyst A. The t-statistic was used to test the null hypothesis that no differences existed between the base case and the case under test.

At the 95% confidence level, four of the six differences were significant in the case of the total insolubles and filterable insolubles, and five of the six differences were significant in the case of the adherent insolubles. Thus, we concluded that operator differences may be a major cause of differences between laboratories.

Overview and General Discussion

The operator factor appears to be a major consideration. Poor reproducibility between laboratories (reported in ASTM D2274) may be a matter of poor reproducibility between analysts. Part of the problem may be the different techniques used by the analysts in those parts of the method that are not defined in detail. Another part of the problem may be the effect of a residue that arises from the adherent insolubles solvent, a residue that could be present in different quantities in solvents used in different laboratories or in the same laboratory at different times.

Further, experienced analysts should be used where the results are critical (e.g., in the acceptance or rejection of a lot of fuel), since experience appears to play a significant role in the spread of data (standard deviation) obtained by an analyst. Moreover, all analysts should be tested periodically on their techniques on standardized fuels, since even an experienced analyst can drift into the use of non-standard practices. Such standardized fuels would consist of a few high quality compounds that represent the major classes found in diesel fuel (saturates, cyclics, olefins, and aromatics). The standardized fuels also could be useful to train a new analyst to run the method according to the written procedure.*

*DTNSRDC is experimenting with the development of standardized fuels. When sufficient data are assembled to provide support for the concept, the ASTM D02 Committee will be requested to consider an annex to ASTM that requires the use of standard fuels to qualify analysts.

PROCESS VARIABLES EFFECTS

Effect of Bath Temperature

Figure 2 shows the responses of the total insolubles level of the three fuels to changes in bath temperature. While the three data points for each fuel do not define the exact nature of the response curves, from them we can estimate the slope of the curves at 95°C (203°F), the standard temperature. The slopes range from 0.14 to 0.40 mg/100 mL/°C. Therefore, if the temperature were controlled within the 0.2°C (32.4°F) specified in ASTM D2274, the effect on the total insolubles would range from less than 0.03 mg/100 mL for Fuel N to about 0.08 mg/100 mL for Fuel A, the most reactive fuel.

Effect of Oxygen Flow Rate

Figure 3 shows the total insolubles responses of the fuels to changes in the oxygen flow rate. The slopes of these curves at the 3.0 L/hr oxygen flow rate specified by ASTM D2274 range from about 0.08 to 0.11 mg/100 mL/°C. These results show that, if the oxygen flow rate were held within the 0.3 L/hr specified, the error in total insolubles would be less than 0.03 mg/100 mL from this effect.

Effect of Time-in-Bath

Figure 4 shows the total insolubles responses of the fuels to changes in the time in the heating bath. The slopes of the curves at the standard 16-hr residence time range from about 0.1 to 0.3 mg/100 mL/hr residence. If the operator were careful to remove the oxidation cells within 15 minutes of the specified 16 hr, the error in the total insolubles from this cause would range from about 0.03 mg/100 mL with the stable Fuel N to about 0.08 mg/100 mL with the least stable Fuel A.

If the maximum observed effects were taken as the potential error from that cause and if these effects were assumed to be cumulative (an unlikely event), the maximum errors caused by failures to hold the specified temperature, oxygen flow, and

residence time at the specified value would be less than 0.2 mg/100 mL. Obviously, if every person who performed the ASTM D2274 procedure would conform to the specified ranges of these variables, the variables would not be major factors in the reproducibility between laboratories.

Effects on Filterable and Adherent Insolubles

Figures 5, 6, and 7 show how changes in bath temperature, oxygen flow rate, and time-in-bath effect the amounts of filterable and adherent insolubles produced in the ASTM D2274 test. The shapes of the curves are similar to the shapes of comparable curves for the total insolubles.

The largest slopes for the filterable and adherent insolubles were determined from each figure. The effects on filterable insolubles formation ranged from 0.04 mg/100 mL for the temperature and oxygen flow effects, to 0.08 mg/100 mL for the 15-minute time deviation. The estimated effects on the adherent insolubles formation ranged from 0.004 (temperature) to 0.024 mg/100 mL (oxygen rate) if these two factors are controlled within the 0.2°C (32.4°F) and 0.3 L/hr specified in the method.

Arrhenius Correlation

The arithmetic scales used in Figures 2 and 5 resulted in curved responses. However, a century ago, Arrhenius used an integrated form of the van't Hoff equation and postulated that the influence of temperature on a chemical reaction could be expressed in the form:

$$\ln k = -[E/RT] + \text{constant.}$$

If the Arrhenius equation applies, a plot of the logarithm of the reaction rate constant versus the reciprocal of the absolute temperature would result in a straight line.

The total insolubles in Figure 8 are assumed to be a measure of the reaction rate constant for the instability reactions involved, and their logarithms are plotted on the y-axis. The reciprocal absolute temperature, K, is used as the x-axis variable. A linear fit is evident for Fuels B and N, but Fuel A shows evidence of curvature. Glasstone⁵ stated that the Arrhenius correlation frequently fails for chain reactions, and some workers in the field feel that instability reactions involve free radicals and chains. However, the curvature also could result from the greater reactivity of Fuel A, because any major consumption of the active compound from which the total insolubles are formed results in a reduced reaction rate. (It is assumed that a first-order reaction dependent on the concentration of the active compound is the first step in the reaction.)

Figure 9 shows a similar plot for the adherent insolubles and for the filterable insolubles produced in Fuel B at various temperatures. Note that the lines are parallel; it may indicate similar mechanisms for the formation of the two types of insolubles. Alternatively, it could indicate that the first step in both reactions is the same and is the rate-determining step. If this was true, then the energy of activation, E, would be the same and the slopes would be identical.

Additional Time-in-Bath Curves

Figure 10, from White,⁴ provides additional information on the effect of time-in-bath. The fuels used to develop the data for these curves were blends of an LCO and an SK distillate in various proportions. The uppermost curve is the reactive LCO and the lowermost curve is the SK stock. The intermediate curves represent blends that contain 15%, 30%, and 40% by volume of the LCO.

Three factors should be noted.

- First, the curves fall in the correct relative positions, but the intermediate curves do not represent additive functions of the two

extreme curves. Something in the SR distillate seems to inhibit the LCO's reactions.

- Second, an ASTM D2274 test of a fuel taken at a single 16-hr residence time can be misleading. Although a stable fuel such as the SR stock may reach close to its maximum content of insolubles, a more reactive fuel such as the 40% LCO blend may meet the specified test limit but produce more insolubles at a longer stress period. Tests at several time periods are needed to obtain sufficient information on a fuel's potential behavior.
- Third, the shapes of the curves are similar to the classical curves for the concentration of the final product in a consecutive first-order reaction. This supports the concept of an intermediate product, such as a hydroperoxide, that has been postulated by past investigations.

Figure 11, also from White,⁴ shows another reason the 16-hr test may be inadequate. The figure shows two LCO stocks. The Gulf-coast stock is the same as that shown in Figure 10. This fuel's total insolubles content at the 16-hr point exceeded the 1.5 mg/100 mL total insolubles permitted by MIL-F-16884H for the Navy's ship fuel. The West-coast fuel produced modest amounts of insolubles for over 16 hr; after about 24 hr, it began to produce profuse amounts of insolubles and rapidly passed the level attained by the Gulf-coast LCO. The West-coast fuel contained almost four times the insolubles attained by the Gulf-coast LCO after about 60 hr of stress.

FINDINGS, CONCLUSIONS, AND RECOMMENDATIONS*

ITEMS DERIVED FROM THE QUESTIONNAIRE

1. (F) The ASTM D2274 procedure is not followed exactly by most analysts. Local variations that are "just as good" exist in the laboratories of most respondents to the questionnaire. The following are major areas of deviation.

- The use of nonstandard filtration systems.
- The use of solvents other than those specified.
- The use of solvents with a lower quality than the standard.

2. (R) The ASTM D2274 procedure should be rewritten to provide more guidance to the analyst and to explain the importance of the more critical steps in the procedure.

ITEMS DERIVED FROM OPERATOR DIFFERENCES

1. (F) The experience of the analyst is a critical factor in determining the spread of data obtained in replicate determinations and the resultant standard deviation. The standard deviation of an experienced analyst may be a sixth of that of an inexperienced analyst.

2. (F) The idiosyncracies of the individual operator are critical in determining the mean value of replicate determinations on the same fuel.

3. (C) Operator idiosyncracies may play a major role in the large values of the reproducibility between laboratories associated with the method. It is essential to reduce differences in the techniques used by the analyst.

4. (R) In addition to rewriting the procedure to emphasize critical procedural steps, ASTM should incorporate an annex to the method that enables

*For the purpose of this report, a finding is a fact obtained experimentally or by other investigation. A conclusion involves a logic process such as the development of a correlation based on a number of findings. A recommendation indicates what the author thinks is required. These three types of results are indicated by (F), (C), and (R).

analysts (e.g., through the use of standard fuels) to check their technique and supervisors of quality control laboratories to test their analysts.

ITEMS DERIVED FROM A STUDY OF SPECIFIED VARIABLES

1. (F) Deviations in the insolubles formed in the ASTM D2274 test are negligible when the operating temperature and the oxygen flow rate are kept within the specified limits (i.e., within 0.2°C (32.4°F) of the specified 95°C (203°F) temperature and within 0.3 L/hr of the specified 3.0 L/hr oxygen flow rate), and when the time-in-bath does not deviate by more than 15 minutes from the specified 16-hr period.

2. (C) Deviations in temperature, oxygen flow rate, and time-in-bath, if kept within the ranges indicated above, do not explain the wide deviations in insolubles reported by different laboratories testing the same fuel.

3. (F) The shapes of plots of total insolubles versus time-in-bath vary widely among fuels. The curves start to rise almost immediately for some fuels; other fuels may experience an extended induction period before profuse amounts of insolubles begin to form.

4. (C) A measurement of the amounts of insolubles formed in a fuel subjected to an accelerated test such as the ASTM D2274 method at a single point in time is inadequate to define the storage stability of that fuel.

5. (R) A method that uses more than one point in time should be developed and correlated with results obtained with ambient storage or with storage at 43°C (109.4°F). (A good correlation exists between ambient and 43°C (109.4°F) storage results.)

6. (F) An Arrhenius-type plot (the logarithm of the total insolubles versus the reciprocal of the absolute temperature) tends to yield a straight line for three fuels examined. However, the slopes of those lines were not all the same.

7. (F) In the case of one diesel fuel, an Arrhenius-type plot of filterable, adherent, and total insolubles yielded parallel straight lines.

8. (C) The reactions that lead to the formation of filterable insolubles and adherent insolubles are possibly similar or even identical, because the activation energies, which are related to the Arrhenius slope, are identical.

ACKNOWLEDGMENTS

The author wishes to thank Messrs. V. Cadorette, E.D. Grant, F. Gomba, J. Cosby, and R.J. Bowen for furnishing the laboratory data used in this report. Appreciation is also due Drs. M.D. Klinkhammer and R.E. Morris for permission to use figures on time-in-bath versus total insolubles obtained on light-cycle oil blends.

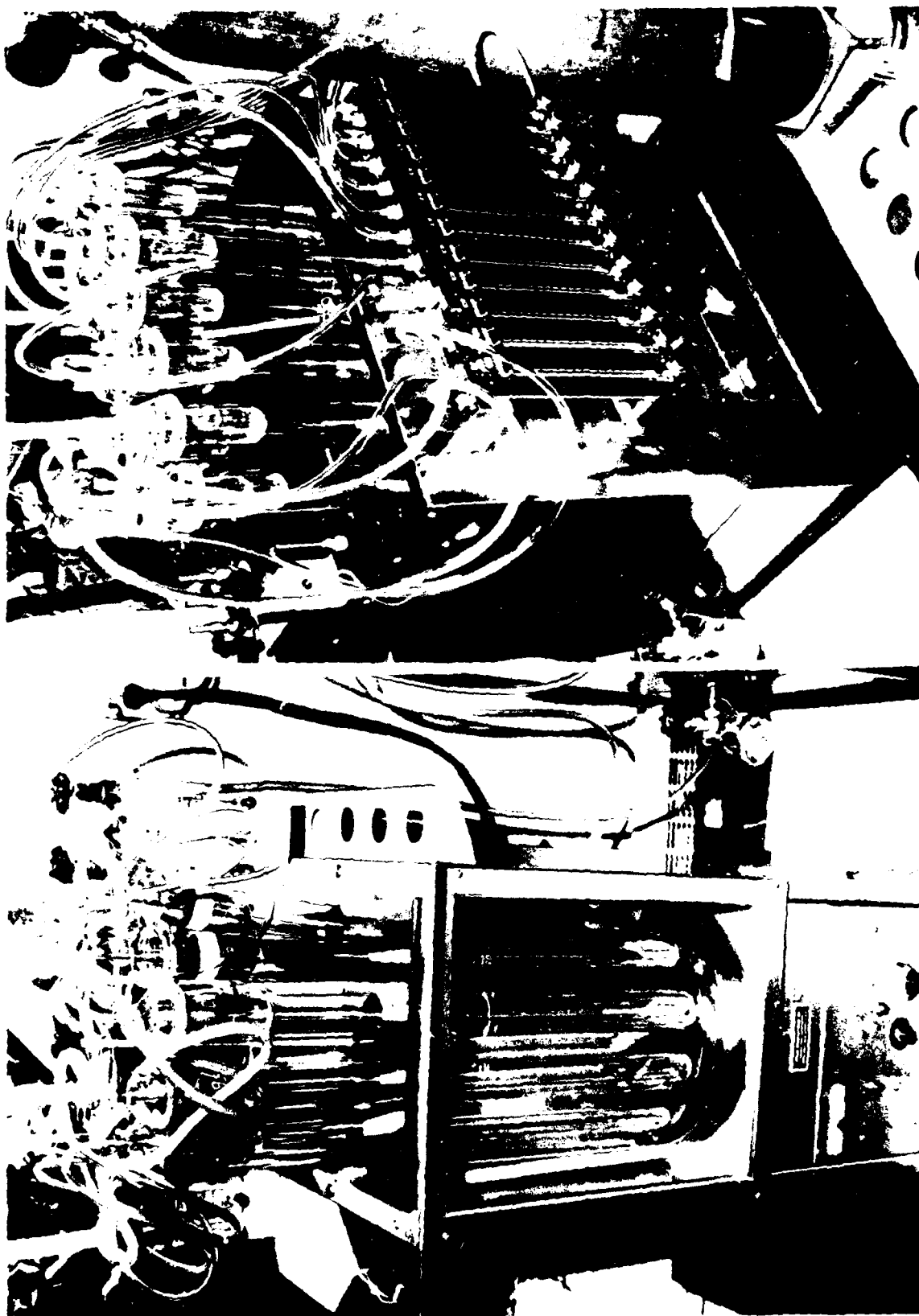


Fig. 1a. Light-cell oxidation apparatus.

Fig. 1b. Twelve-cell oxidation apparatus.

Fig. 1. Oxidation units.

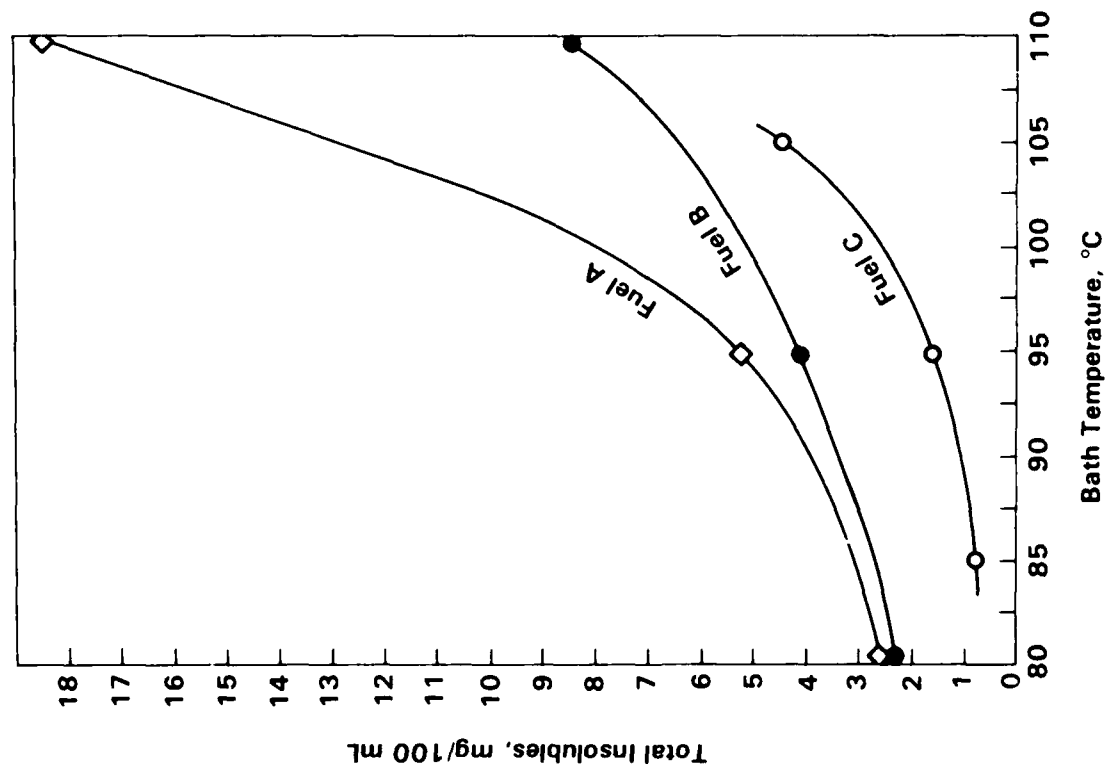


Fig. 2. The effect of bath temperature on the formation of total insolubles in three fuels after 16 hr at temperature with an oxygen flow rate of 3 L/hr.

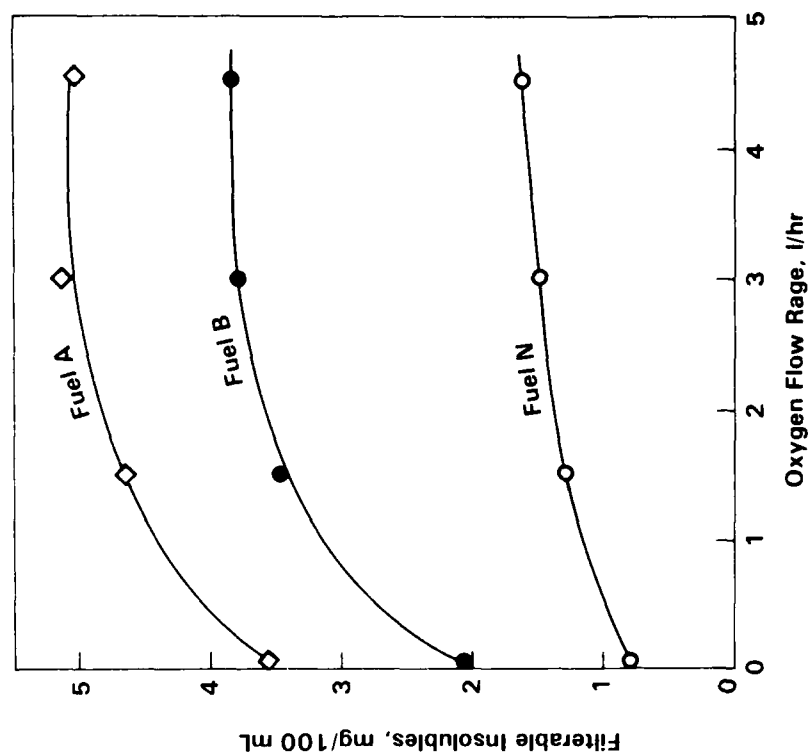


Fig. 3. The effect of oxygen flow rate on the formation of total insolubles in three fuels held at 95°C for 16 hr.

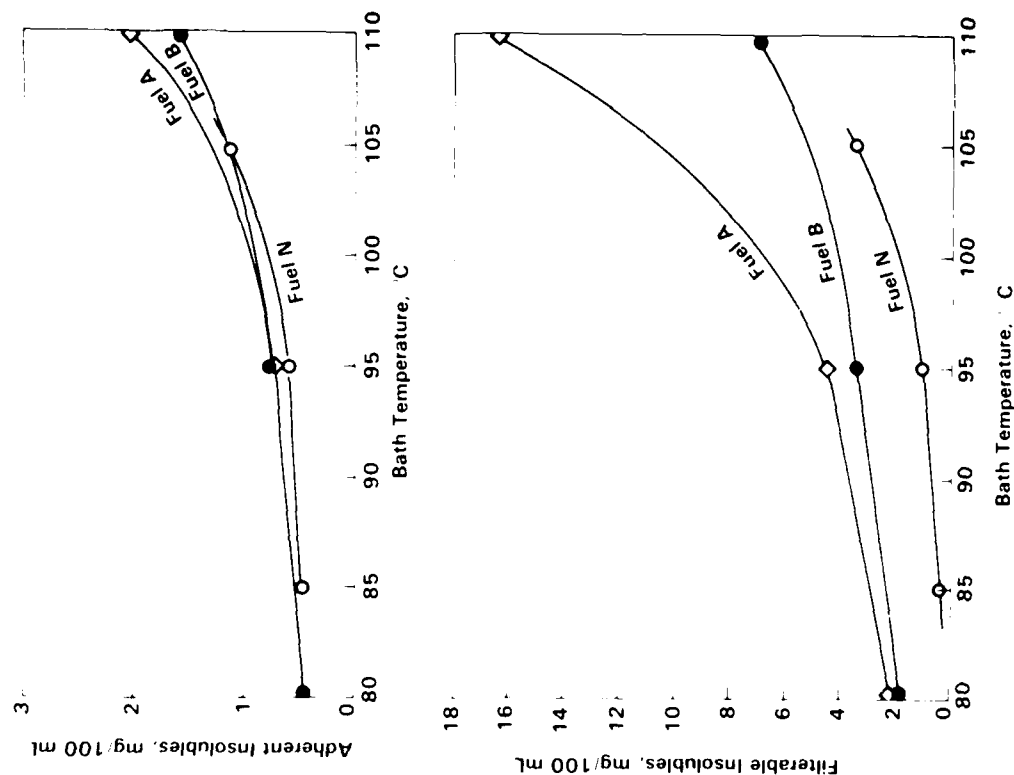


Fig. 5. The effect of bath temperature on the formation of adherent and of filterable insolubles in three fuels held in the temperature bath for 16 hr while 3 L/hr of oxygen passed through the fuels.

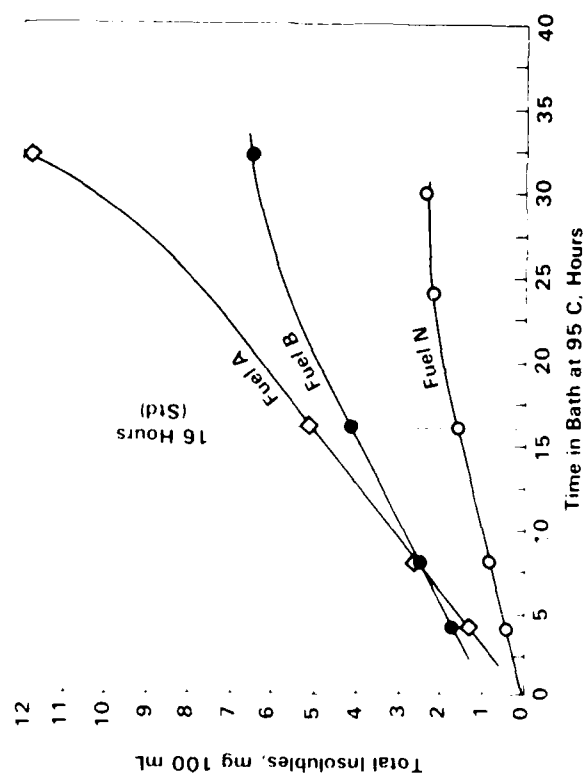


Fig. 4. The effect of time-in-bath on the formation of total insolubles in three fuels held in a 95°C bath while oxygen was passed through the fuel at a rate of 3 L/hr.

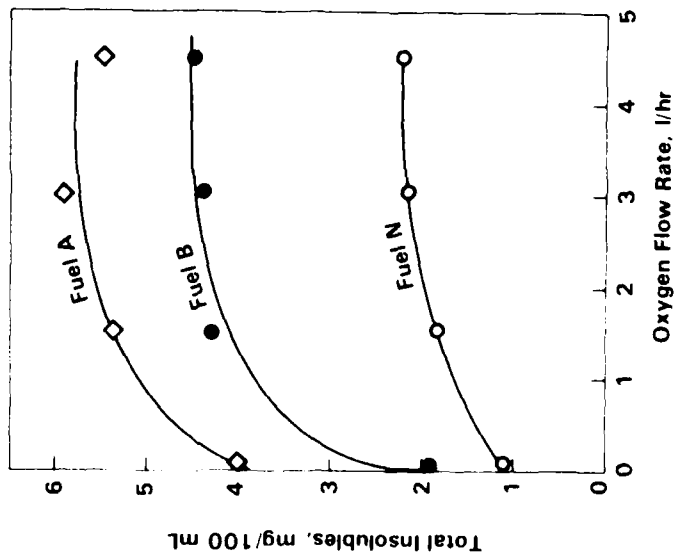
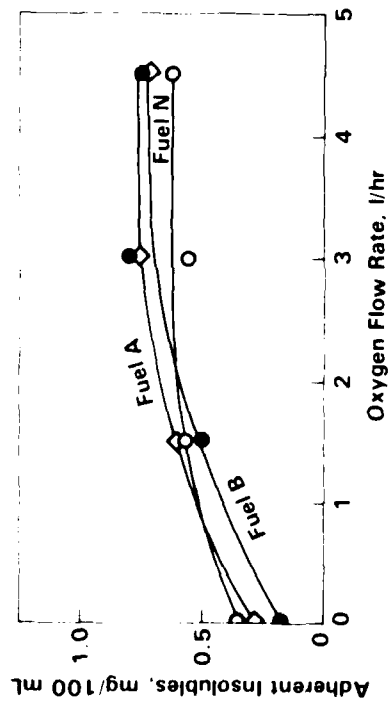


Fig. 6. The effect of oxygen flow rate on the formation of filterable and adherent insolubles in three fuels held at 95°C for 16 hr.

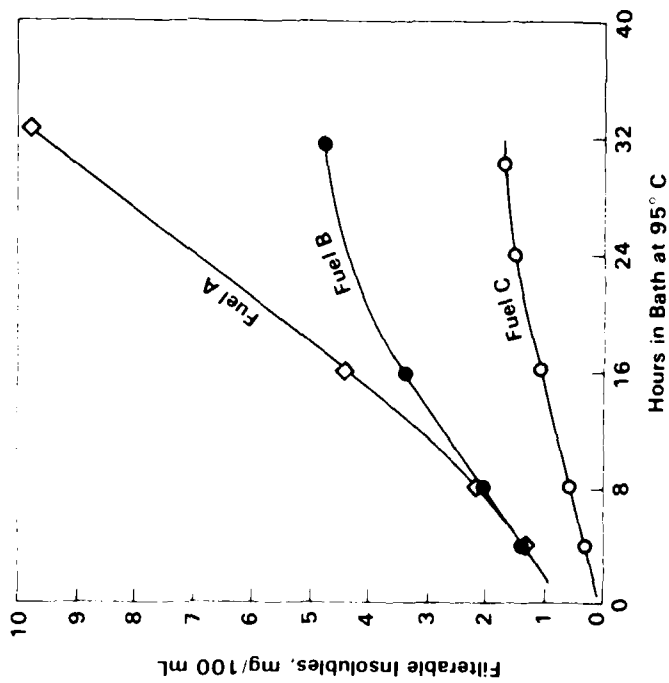
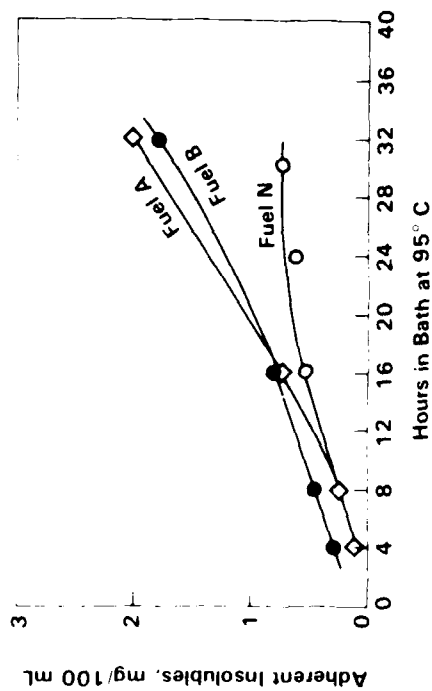


Fig. 7. The effect of time-in-bath on the formation of filterable and adherent insolubles in three fuels held at 95°C while oxygen was passed through the fuels at 3 l/hr.

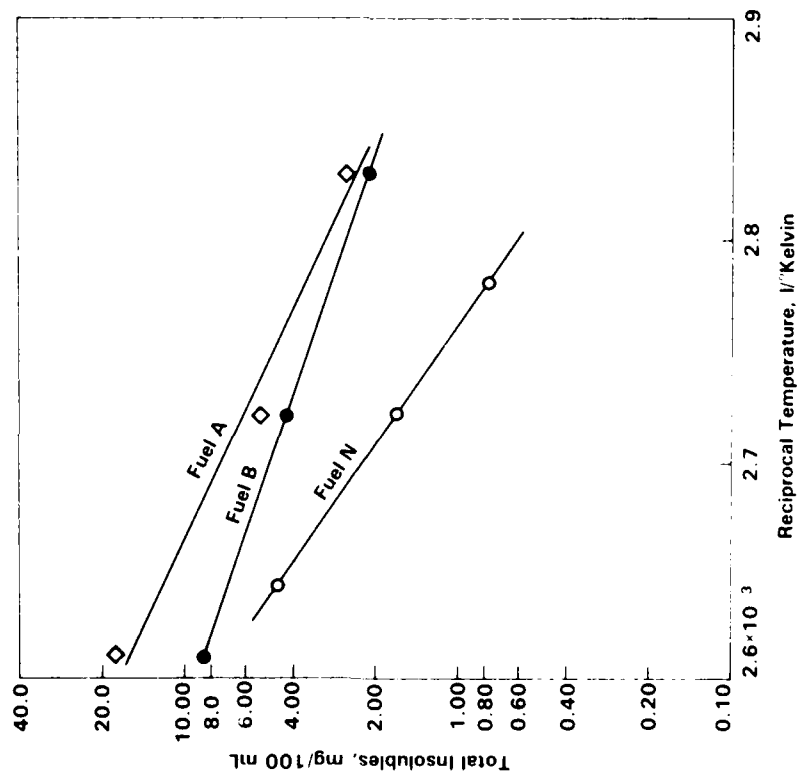


Fig. 8. A test of the Arrhenius relationship; plots of the logarithm of the total insolubles formed in three fuels as functions of reciprocal absolute temperature.

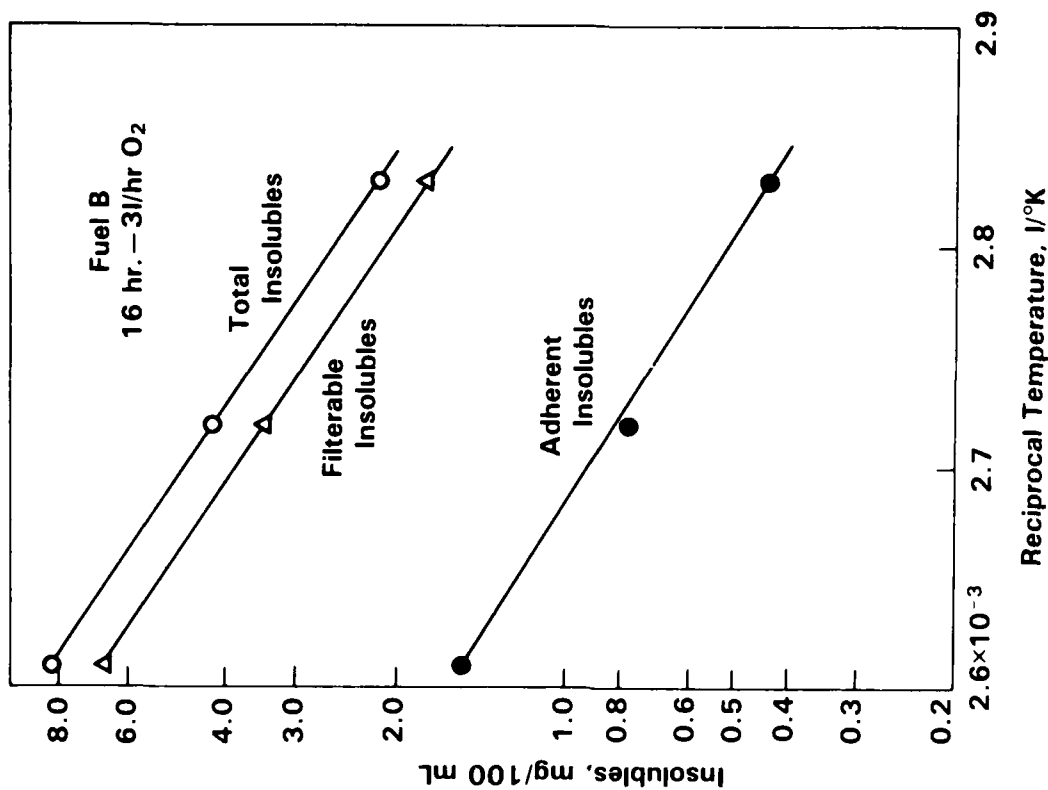


Fig. 9. An application of the Arrhenius correlation to the formation of filterable and adherent insolubles as well as total insolubles in Fuel B.

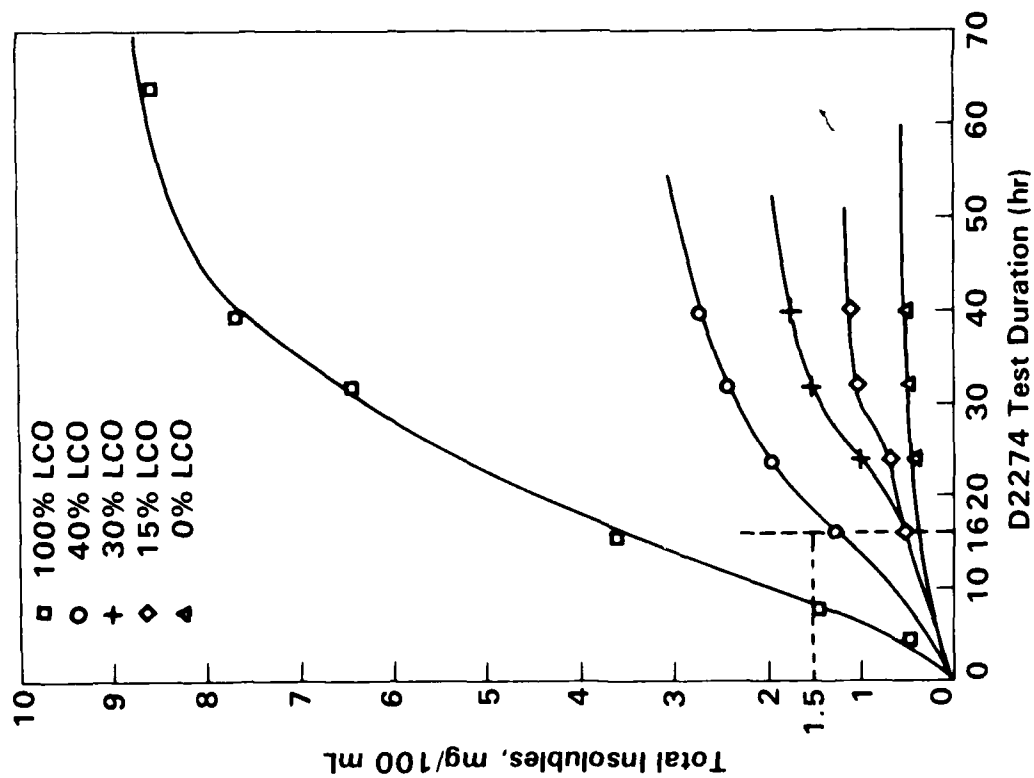


Fig. 10. The effect of the D2274 test duration on the formation of total insolubles in five blends of Gulf-coast light-cycle oil and straight run distillate.

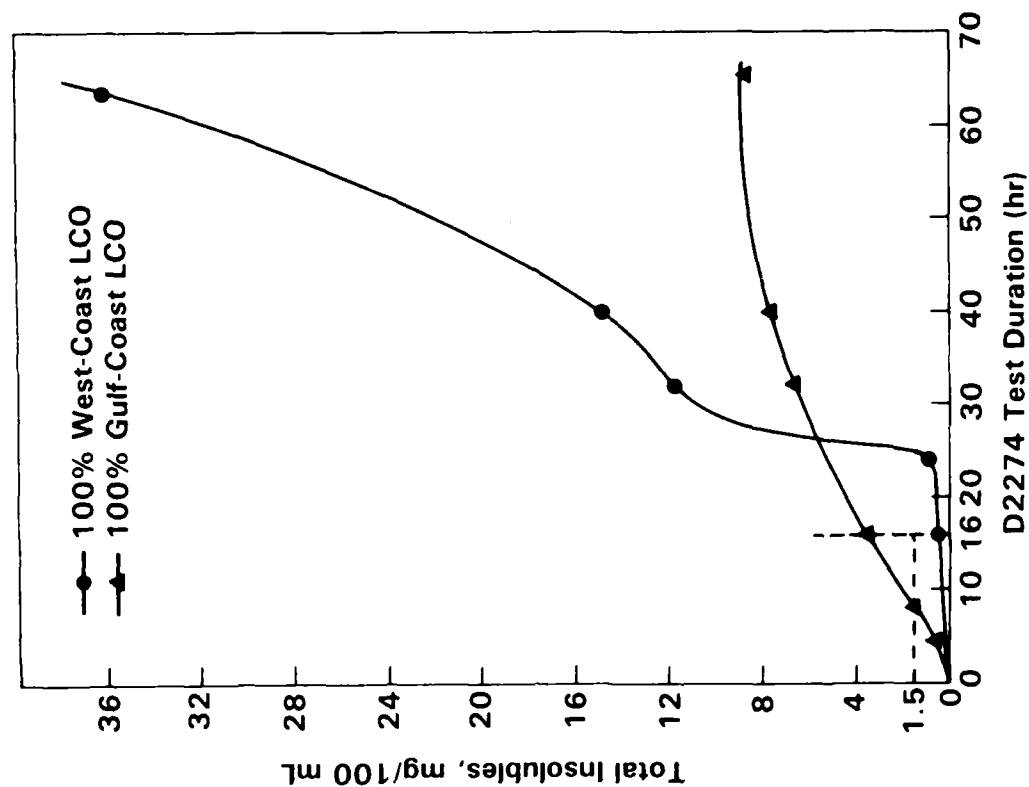


Fig. 11. The effect of D2274 test duration on total insolubles formation in two light-cycle oils, one from the Gulf coast and one from the West coast.

APPENDIX A
QUESTIONNAIRE ON THE USE OF THE ASTM TEST FOR
OXIDATION STABILITY OF DISTILLATE FUEL OIL
(ACCELERATED METHOD - D2274)

1. The purpose of this questionnaire is to identify differences in the interpretation and practice of the D2274 test method, to help identify possible reasons for the poor reproducibility of results between laboratories.

2. Please do not presume the test personnel, whether they are chemists or technicians, are following the procedure exactly. Shortcuts develop in all laboratories and become established as the standard procedure. Experienced operators are certain they remember the necessary details of the procedure, and do not refresh their memories at frequent intervals. Therefore, please do make measurements, observe techniques, read labels, etc. as requested in the following questions. If you are uncertain or passing on answers from the operators, please indicate the fact. Do question the operators about their techniques, if you are not the individual making the test personally. We want to know what is actually done in running the test, not a rehash of what the method says should be done. To the extent possible, answer the questions with respect to one particular recent distillate fuel that has been tested in your laboratory.

3. Please complete the questionnaire and mail prior to 11 October 1983 to:

Dr. E.W. White (Code 2832)
David Taylor Naval Ship R&D Center
Annapolis, MD 21402

Adherence to this target date is strongly urged to allow time for an analysis of the responses prior to the Stability Workshop on 18 and 19 October 1983.

D2274 QUESTIONNAIRE

1. Respondent Information

Name of respondent _____
Position _____
Name and address of laboratory _____
Are you a member of ASTM D-2 Section E-V? _____

2. Sample Information

Answer the following with respect to any distillate fuel sample that has been run at your laboratory. Answer subsequent questions with respect to how the test was applied to this specific fuel.

- a. Type of fuel (1) No. 2 _____ (2) Diesel _____ (3) Other _____
- b. How old was the sample when tested? _____
- c. How was the sample obtained? _____
- d. In what kind of container was it received? _____
- e. Where was the sample stored between receipt and testing, and at what temperature was it stored? _____
- f. Was the sample stored under nitrogen? _____

3. Information on Reagents and Materials

Please furnish the following information by direct reading of labels on the containers in which the reagents were received.

- a. What purity and brand of oxygen did you use? _____
- b. What make, grade, size, etc. of filter paper did you use? _____

- c. What source, brand, and grade of "hydrocarbon solvent" did you use? _____

Was the solvent isooctane? _____
Did you prefilter it as specified? _____
- d. What was the source, brand, grade, etc. of each solvent used in the preparation of the "adherent insoluble solvent?"
 - d-1. Acetone _____
 - d-2. Methanol _____
 - d-3. Benzene _____
(or) Toluene _____

4. Information on Oxidation Cell

- a. Did the cell conform exactly to D2274 Fig. 1? _____
- b. Were the cells used for the duplicate determinations new? _____
Used? _____ One new, one used? _____ Don't know _____
- c. If either cell was new, did you follow paragraph 7.1 exactly? _____
Did you use chromic acid? _____ If not chromic acid, what? _____
What was the soak time? _____ How many times was cell rinsed with
tap water? _____ With Distilled Water? _____ With Acetone?
_____ How was cell dried? _____
- d. If either cell was used, did you follow paragraph 7.2? _____
What detergent did you use? _____ How much precipitation naphtha
did you use? _____ Did you use a substitute for precipitation
naphtha? _____ If so, what was it? _____
- e. Was the oxidation cell, including the oxygen delivery tube and the glass
condenser, constructed of borosilicate glass? _____

5. Information on Preparing the Gooch Crucibles

- a. How did you clean the Gooch? _____
- b. Of what material was the Gooch made? _____
- c. What was the brand or source of the Gooch? _____
- d. What size number Gooch did you use? _____
- e. What were its diameters? At top? _____ At bottom? _____
- f. How many holes and what size holes in the bottom? _____

- g. Did you measure the volume of isooctane used in cleaning glass-fiber filter
disks? _____ How much did you use? _____
- h. How long were Gooch crucibles dried in the oven? _____
- i. How long were they left in the desiccator? _____
- j. Did you use one, two, or three filter disks? _____

6. Information on Starting the Test

- a. How much fuel did you filter, ml.? _____ Was this for more than one
oxidation cell? _____ If so, how many cells? _____

- b. How much time passed after filtering the fuel before the cell(s) was placed in the bath? _____
- c. In filtering the fuel, did you use the set-up of Fig. 2 of the D2274 method? _____ If not, how did you do the filtering? _____
- _____

7. Information on the Temperature Stress Period

- a. How long was the fuel in the bath? _____ Exactly 16 hours? _____
- b. Please record the following information during any test.
- (1) Bath temperature _____ How long after start? _____
- (2) Oxygen flow rate _____ How long after start? _____
- (3) Fuel temperature _____ How long after start? _____
- (4) Room temperature _____ What time of day? _____
- (5) Barom. pressure _____ How long after start? _____
- (6) Relative humid. _____ How long after start? _____
- (7) Bubbles of oxygen/minute (if attainable) _____
- Was a frit used? _____
- (8) Months since last oxygen flowmeter calibration? _____

8. Information on the Cooling Period

- a. How long did it take to remove all tubes from bath? _____
- b. Where did you store tubes for cooling? _____
- c. What was the ambient temperature during cooling? _____
- d. What was the fuel temperature after 4 hr. cooling? _____
- e. Did you have to allow a longer period? _____ How much? _____

9. Information on Filtration for Filterable Insolubles

- a. What was the temperature in the filtration room? _____
- b. How did you clean the separatory funnel? _____
- c. Did you use the self-feeding system of Fig. 2? _____
- d. How many times did you rinse with hydrocarbon solvent? _____
- How much did you use each time? _____ What was your method to contact all parts of the tube? _____

- e. How much solvent did you use for rinsing the following:
The glass funnel? _____ The separatory funnel? _____
The oxygen delivery tube? _____ The outside of Gooch? _____
- f. How long did it take to complete the filtration? _____
- g. How long did you dry the Gooch in the oven? _____
- h. What was the measured oven temperature? _____
- i. What was the weight of the crucible plus insolubles? _____ gm.

10. Information on Adherent Gum Procedure

- a. What volume of adherent gum solvent was used? _____ ml.
- b. Was this used in a single rinse? _____ How Many? _____
- c. What technique was used to contact all surfaces? _____

- d. After the last rinse, was there any evidence, e.g. residual color, that all the gum might not have been removed? _____
- e. Did you use the ASTM D381 air jet apparatus? _____
If not, how did you evaporate the solvent? _____

- f. How did you prevent scale and other debris from the compressed air system from reaching the jet apparatus? _____

- Was the air filtered? _____ How? _____

11. Information on Repeatability and Reproducibility

- a. In view of the rather poor repeatability of the method, do you normally () or occasionally () run duplicate determinations?
- b. If you do run duplicates, what is the usual difference between results for filterable insolubles? _____ Adherent gum? _____
Total insolubles? _____
- c. Does the repeatability of duplicates seem to you to depend on the level of the insolubles? _____
- d. What, in your opinion, is the cause of the very poor reproducibility among different laboratories? _____

12. Information on the Laboratory

- a. Are the different parts of the test (filtering, temperature stressing, weighing, jet evaporation, oven drying) conducted in the same room?

- b. Are the locations where the test is run exposed to daylight, particularly to direct sunlight? _____

- c. Are lab temperatures the same summer and winter? _____

How much variation in temperature is there between (1) day and night?

_____ (2) summer and winter? _____

- d. Is the fuel subject to exposure to sunlight during any part of the test?

_____ Explain _____

Name of person completing the questionnaire _____

Are you the person who runs D2274 tests personally? _____

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